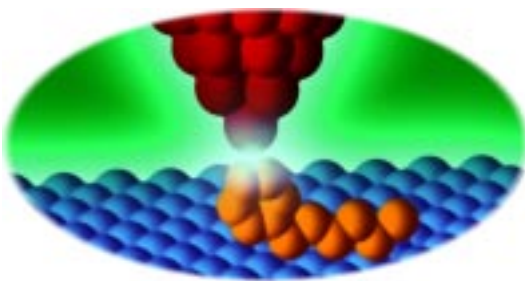


2.4 Nanotechnology



The need for improved spatial resolution currently limits the ability of industry to answer key questions regarding the chemical composition of surfaces and interfaces. Needs range from improved chemical and structural diagnostics to phase identification and trace compositional analysis. In addition to meeting current industry needs in these areas, there is a continuing demand for new measurement methods to be developed that will be positioned to meet emerging measurement challenges. NIST/CSTL develops measurement tools

that enable chemical characterization of elements, isotopes, and molecules at millimeter to nanometer spatial scales with major, minor, and trace concentrations. These tools are developed such that the “microspatial” relationships can be correlated with specific macroscopic properties.

Phase Identification from Sub 200-nm particles by Electron Backscatter Diffraction (EBSD)

J.A. Small (837)

The signal-to-noise ratio of electron backscatter diffraction measurements for particles in the submicrometer range is limited by electron scatter from areas of the sample other than the particle of interest. We have developed a sample holder to enable particle mounting on a thin, electron transparent, substrate that reduces the noise contribution from electrons that scatter into the substrate and thus improves pattern quality from particles less than 300 nm in size. The use of other thin-film compositions and low accelerating voltages may extend the application of EBSD phase identification to particles less than 100 nm in size.

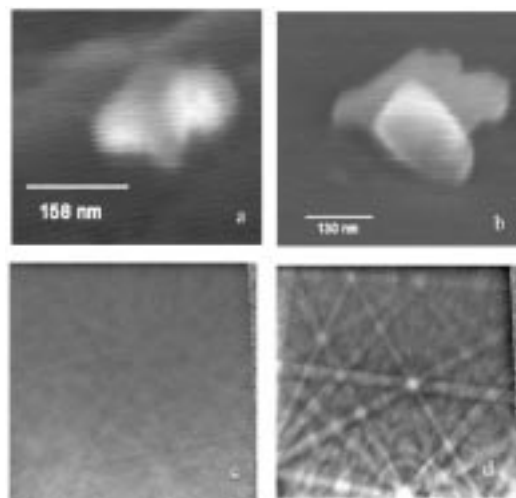


Figure (c) is the EBSD pattern from a 160 nm Al_2O_3 particle mounted on a bulk carbon substrate (a). Figure (d) is the EBSD pattern from a 150 nm Al_2O_3 particle mounted on a 20 nm carbon thin-film (b). The quality of the EBSD pattern from the particle mounted on the thin substrate is clearly superior to the pattern from the particle mounted on the bulk substrate and has a high enough signal-to-noise ratio to conduct a phase identification analysis of the particle and identify it as hexagonal Al_2O_3 .

Fabrication and Electron Microprobe Characterization of Barium-Strontium-Titanate (BST) Film

R.B. Marinenko, J. Armstrong (837), D.L. Kaiser, J.J. Ritter, P.K. Schenck, C. Bouldin, J.E. Blendell, and I. Levin (MSEL)

The electron probe microanalyzer (EPMA) was used to quantify the composition of 5 nm to 400 nm thick BST films. Accurate and reproducible quantitative analysis of films with thicknesses greater than 20 nm can be done readily. But the analysis of films that are only a few nanometers thick are more difficult to quantify with EPMA due to the low x-ray count rates resulting from the very small sample volumes.

Three commercial BST films (54 nm, 75 nm, and 400 nm thick) on Si or Pt/Si substrates prepared by sputtering or MOVCD were analyzed. Eight films prepared at NIST (5 nm to 100 nm thick) were also analyzed. Uncertainties in the EPMA data taken from the randomly selected points on each specimen were approximately 2% relative or less for films in the range of 40 nm to 400 nm, but these uncertainties increased to as much as 20% relative for films less than 20 nm thick. Improvements in statistics for the thinner films will be needed for EPMA to be useful for characterizing the thinnest films. Other materials proposed for gate oxide layers, such as the oxides of zirconium, hafnium, and aluminum and silicon oxynitrides may be evaluated with EPMA.

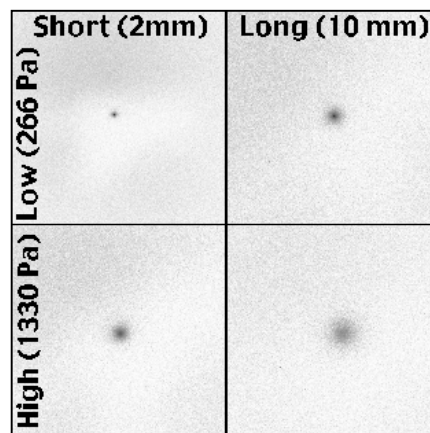
BST is one of a few high dielectric materials considered for the *next generation gate dielectric layers* where thicknesses down to 1 nm will be required. Since the properties and performance of these materials are strongly dependent upon thickness and composition, analytical methods that can determine these characteristics accurately are critical.

Phosphor Imaging Plate Measurements of Primary Electron Beam Broadening in the Environmental Scanning Electron Microscope

S.A. Wight and C.J. Zeissler (837)

The resolution of the environmental scanning electron microscope (ESEM) is limited by the scattering of primary electrons out of the electron probe. Since it is critical to understand the size and magnitude of the electron skirt to test simulations and generate correction schemes, we have developed a method to directly measure electrons scattered out of the primary electron beam as a function of vacuum and instrument conditions, using phosphor imaging plate technology.

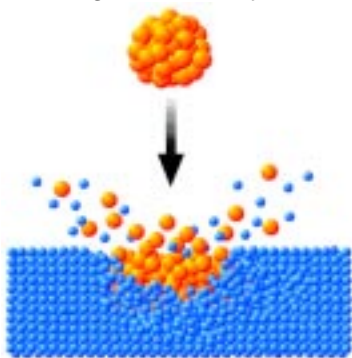
Graphical representation of the primary and scattered electrons at short and long beam-gas path-length and high and low pressures of water.



Fundamental Studies of Mechanisms in Molecular SIMS Using Cluster Projectiles

G. Gillen (837)

The high sensitivity, monolayer sampling depth, and high spatial resolution of secondary ion mass spectrometry (SIMS) make it a promising technique for industrial applications in polymer surface characterization, biomolecule analysis and evaluation of organic surface contamination. We are evaluating new approaches for organic surface analysis using energetic cluster bombardment (Cluster SIMS) and attempting to develop a fundamental understanding of the mechanisms of cluster-organic surface sputtering in order to optimize the technique. Compared to conventional SIMS, the use of small cluster primary ion beams, such as C_8^+ , can enhance molecular secondary ion signals by several orders of magnitude as well as reduce beam-induced damage in some materials. We have found that optimal secondary ion yields and minimal accumulation of damage are obtained by using cluster ions in the range from C_6^+ to C_8^+ . Computer modeling of the cluster-surface interaction indicates that the reduction in damage accumulation is primarily related to the dissociation of a cluster ion after impact with the surface leading to a significant reduction in the depth of the altered layer below the sputtered surface. Furthermore, recent experiments suggest that the enhancement in secondary ion signal under cluster bombardment results from the much higher fraction of intact molecules that survive the cluster impact event. These fundamental



studies will eventually lead to a robust new method for organic surface analysis that could be transferred to US industry.

Ultra Shallow Depth Profiling by ToF-SIMS

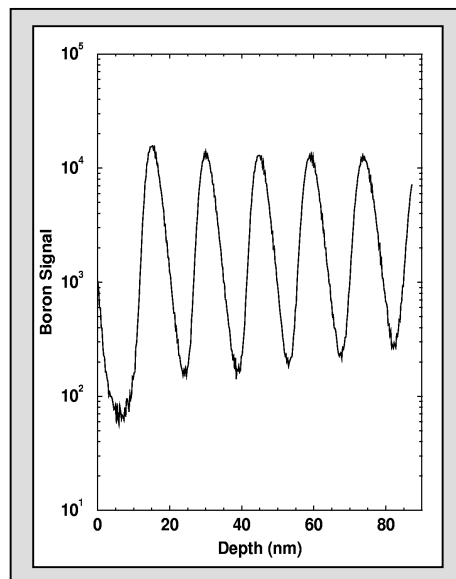
A.J. Fahey and S.V. Roberson (837)

The operating parameters and the capability of time-of-flight secondary ion mass spectrometry (ToF-SIMS) are being evaluated for depth-profiling analysis of nanometer-scale boron implants in silicon wafers.

Reductions in the scale of semiconductor devices require SIMS measurements with depth resolutions on the nanometer scale.

Using the NIST ToF-SIMS that is equipped with two ion sources, the boron signal in boron-doped silicon was measured where the boron was deposited in near-monolayer planes separated

by 15 nm. Using a pulsed Ga⁺ ion beam and SF₅⁺ ions for the sputtering beam, resolution as a function of depth ranged from 1.45 nm to 1.66 nm, consistent with previous measurements. However, the dose for the analyzing beam can be high under depth profiling conditions and can lead to a degradation in resolution. Thus, care was taken to reduce the Ga⁺ dose, but this had the consequence of making analysis times longer than desirable for industrial application of ToF-SIMS for depth profiling.



Depth profile of boron delta structure.

Depth Profiling of Organic Films using the Time-of-Flight SIMS

S.V. Roberson (837)

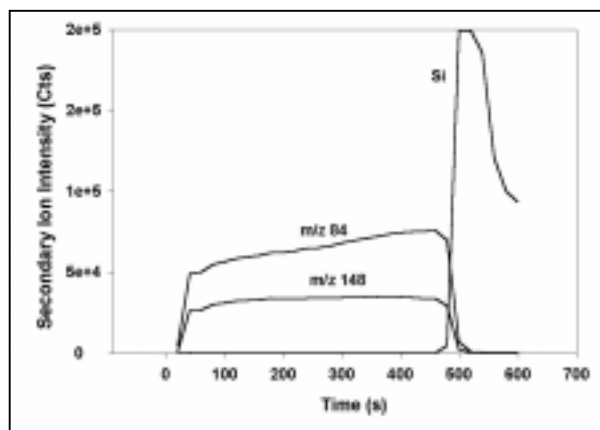
Researchers in the CSTL's Surface and Microanalysis Science Division are optimizing the parameters for analysis and erosion in depth profiling of organic films by using a dual beam approach with time-of-flight SIMS. In



this method, a low-energy sputter gun erodes a square crater in the sample while a second, pulsed ion gun is used to analyze a small region in the center of the sputtered crater.

This dual-beam

approach was investigated in terms of its usefulness for studying positive molecular ion emission from thin films of glutamate and PMMA on silicon substrates. The method should be useful for profiling of ultra thin layers and for interface analysis.

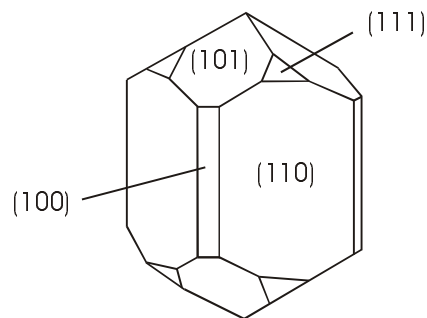


Dual beam depth profile of a glutamate thin film.

Characterization of the Morphology of Voids in Rutile Nanoparticles

S. Turner (837)

The Surface and Microanalysis Science Division is characterizing the morphology of voids in rutile nanoparticles using transmission electron microscopy (TEM) and selected area electron diffraction (SAED). The characterization of nanoparticle morphology relative to crystallographic orientation is challenging, in part due to the small size of the particles and to difficulties in their manipulation. It is also important since some crystallographic planes in catalyst particles are more reactive than other planes and therefore preferable for promoting some reactions.



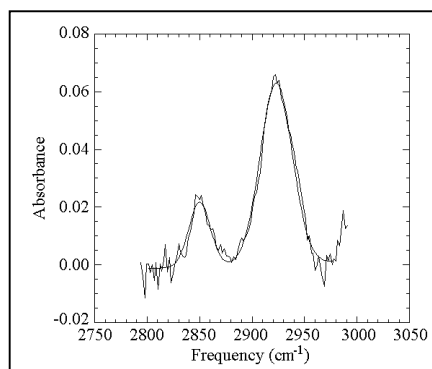
In this study, TiO₂ (rutile) nanoparticles containing voids are characterized. In previous work, it was shown that some rutile nanoparticles generated in a flame burner system contain central inclusions. These inclusions were characterized as voids or cavities using electron holography. Similar cavities have been noted in palladium nanoparticles. The morphology of these faceted cavities is of potential interest in determining volume changes in transformation reactions. If the cavities have reached equilibrium, the morphology is also of interest in determining relative surface energies of crystals. Prior to this work, the morphology of cavities in nanoparticles had not been determined. Our measurements indicated that many of the voids are consistent with a prismatic morphology with dipyramid terminations.

Proposed model for cavities in some rutile nanoparticles.

Absorption Sensitivity and Spatial Resolution in Near-Field Infrared Spectroscopy

C.A. Michaels and S.J. Stranick (837)

The integration of IR absorption spectroscopy into near-field scanning optical microscopy is a promising approach to in-situ, non-destructive, high spatial resolution imaging, with applications in the chemical characterization of materials and nanotechnology. We are assessing absorption sensitivity, attainable spatial resolution, and the sensitivity of near-field IR absorption microscopy to topographic artifacts. Our results indicate that the microscope sensitivity is sufficiently high to allow spectral measurements of samples of sub-wavelength thickness and that near-field absorption imaging may be less sensitive to topographic artifacts than other near-field imaging modes.



The near-field infrared absorption spectrum of a 2 μm thick polystyrene film in the aliphatic C-H stretching region acquired in 1 s.

Analyzing the Tough Ones: Quantitative X-ray Microanalysis of Extreme Topography

D.E. Newbury (837)

Conventional quantitative electron probe microanalysis is restricted to surfaces that are flat to a relief of 100 nm amplitude or less by geometric effects on electron scattering and x-ray absorption. Therefore, conventional quantitative x-ray microanalysis of rough specimens can be severely compromised. We have overcome the surface flatness limitations of conventional quantitative electron probe microanalysis using point beam analysis (the peak-to-local background (P/B) method) that incorporates measures of both

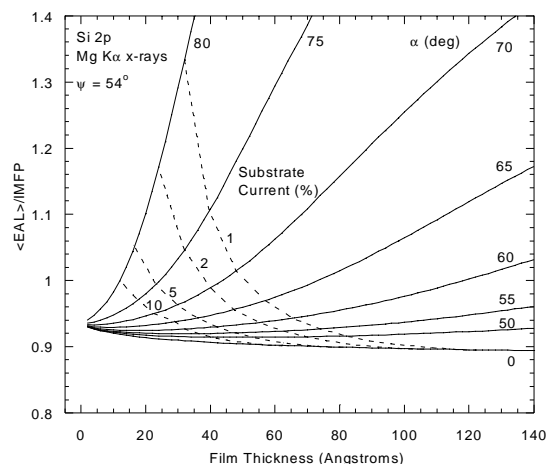
We have overcome the surface flatness limitations of conventional quantitative electron probe microanalysis using point beam analysis.

the characteristic and continuum (bremsstrahlung) x-rays at the same energy. Use of this method on a IN-100 Alloy Sphere (122 μm diameter; screened from EDS) for Al-K, Mo-L, Ti-K, Cr-K, Co-K, and Ni-K produced more than an order of magnitude improvement in relative error in some cases.

Effects of Elastic-Electron Scattering on Measurements of Silicon Dioxide Film Thicknesses by X-Ray Photoelectron Spectroscopy

C.J. Powell (837) and A. Jablonski (Institute of Physical Chemistry)

Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are used extensively in the semiconductor and other industries for determining thickness of thin ($< 10\text{ nm}$) overlayer films on substrates. We are improving the measurement accuracy of these techniques through calculations of the ratio of the effective attenuation length (EAL) for the relevant electron energy and film material to the inelastic mean free path (IMFP). The extent to which the EAL differs from the IMFP has not been previously documented for films of SiO_2 on Si that are of high technological importance. A plot of this ratio versus SiO_2 film thickness (for Mg $\text{K}\alpha$ x-rays and for an XPS configuration in which the angle ψ between the x-ray source and the electron energy analyzer is 54°) for different electron emission angles (α) indicates that the ratio remains constant up to $\alpha = 60^\circ$ (see figure). This work will be extended to other materials for which film thicknesses are determined by XPS or AES.



Analytical Electron Microscopy of Ultrathin Gate Dielectric Films on Silicon

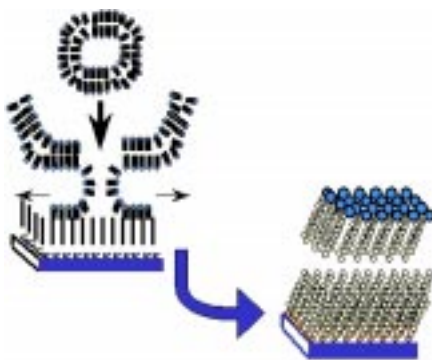
J.H.J. Scott (837)

Details provided in **Microelectronics** section.

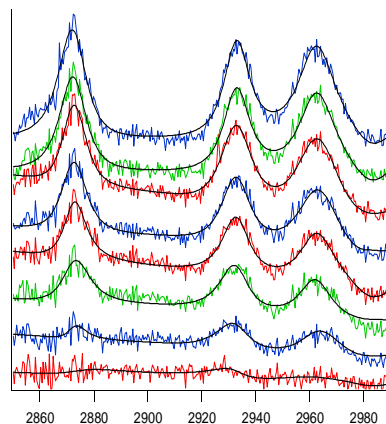
Determination of the Absolute Molecular Orientational Distribution of the Polystyrene Surface

L.J. Richter (837), K.A. Briggman, J.C. Stephenson (PL), and W.E. Wallace (MSEL)

Vibrationally-resonant sum-frequency generation (VR-SFG) employing state-of-the-art femtosecond lasers is being used to develop measurement procedures for the study of polymer thin films that have important roles in many industries including semiconductor devices, automobile coatings, and construction materials. A general technique utilizing optical interferences in thin films has been developed to identify the interface that gives rise to a specific VR-SFG feature. The feasibility of the technique has been demonstrated through the study of the orientational distribution of the phenyl rings at the interfaces of polystyrene (PS) films spin cast onto oxidized Si substrates. This work was the first to establish the complete orientational distribution for a pendant side group at a polymer surface.



Selected VR-SFG spectra recorded during the HBM formation.



Scanning Tunneling Microscope (STM) Spectroscopy of Atomically Engineered Surfaces: Kondo vs. Non-Magnetic Systems

J.W. Gadzuk and M. Plihal (837)

We are seeking to understand and theoretically quantify STM spectroscopic measurements of solid surfaces containing isolated adsorbed atoms and/or single-atom-by-atom-tailored surface nanostructures. Resonance tunneling STM studies of transition metal atoms adsorbed on noble metal surfaces, some combinations forming Kondo systems, have recently been reported. The important additional influence of artificially-synthesized boundaries such as other atoms, quantum wires, and quantum corrals on the surface is also receiving much attention in the electronics and information technology industries. The spectroscopic results are given as spatially-dependent differential conductance versus voltage spectra, usually observed as asymmetric Fano lineshapes. Temperature and tip-position-dependent tunneling characteristics have been obtained for Kondo systems such as Co or Ce adsorbed on the (111) face of Au and some characteristic results of differential conductance vs. energy have been obtained for several transverse tip positions. Future work will address issues such as the relative importance of ballistic versus quantum vs. chaotic transport within both quantum corrals and other novel nanostructures, as potentially revealed in STM spectroscopic measurements.

The important additional influence of artificially-synthesized boundaries such as other atoms, quantum wires, and quantum corrals on the surface is also receiving much attention in the electronics and information technology industries.

Theoretical Studies of Electrical Conductance in Molecular Wires

C.A. Gonzalez (838) and A. Roitberg (831)

There is a need to develop robust theoretical and experimental tools that can be used on a routine basis in the design of materials that can potentially be used to design efficient electronic components at the nanoscale level. This requires an understanding of the fundamental mechanisms governing electrical conductance in materials at the molecular level (i.e., molecular electronics). We are examining the electronic transport of molecular wire circuits using two of the most commonly accepted theoretical methods for the computation of the couplings (orbital splitting and time-independent Landauer scattering formalism) on the prototype system H-S-(CH=CH)_n-S-H (with n = 3,4,5,7) placed between two singlet H₂Si radicals simulating the donor and acceptor electrodes (reporter groups). Computational results were found to be in excellent agreement with experimental data. We are now extending the theory to improve the description of the molecule-metal junction.

There is a need to develop robust theoretical and experimental tools that can be used on a routine basis in the design of materials used to design efficient electronic components at the nanoscale level.

Flow Imaging Techniques for Characterization of Microfluidic Systems

L. Locascio, E. Waddell, T. Johnson, G. Kramer (839), M. Gaitan (EEEL), D. Ross, R.E. Cavicchi, S. Barker, and M. Tarlov (836)

Details provided in **Chemical and Biochemical Sensing** section.